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(54) Title: PAINT OR COATING COMPOSITION AND METHOD FOR PAINTING OR COATING SURFACES (57) Abstract Steel surfaces and ballast tanks, cargo holds, cofferdams, bridge undersides, the interior of offshore legs, ship hulls, ship cabin walls, ship decks, aircraft landing areas on ships or offshore constructions, drinking water tanks, underseals for containers, etc., are painted or coated by applying a composite material, which on curing, forms a material comprising a matrix comprising: A) homogeneously arranged inorganic solid particles of a size of from about 50 Å to about 0.5 µ, or a coherent structure formed from such homogeneously arranged particles; and B) densely packed solid particles having a size of the order of 0.5 - 100 µ and being at least one order of magnitude larger than the respective particles stated under A), or a coherent structure formed from such densely packed particles, the particles (A) or the coherent structure formed therefrom being homogeneously distributed in the void volume between the particles (B), the dense packing being substantially a packing corresponding to the one obtainable by gentle mechanical influence on a system of geometrically equally shaped large particles in which locking surface forces do not have any significant effect; and allowing the paint or surface coating composition to cure to form the above-defined matrix. Particles (B) are preferably Portland cement, particles (A) are preferably silica dust generated by growth from a vapour phase such as silica dust produced as a by product in the production of ferrosilicium or silicium metal in electrical furnaces. Homogeneous distribution of particles (A) is obtained by means of a surface active dispersing agent such as a concrete superplasticizer. Paint for use in the above method and generally for painting or coating any marine, offshore or landstructure to be coated and/or protected comprises above consti- tuents and an organic binder such as a water-based emulsion, and optionally a defoamer and/or a thixotropic agent.		

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PAINT OR COATING COMPOSITION AND METHOD FOR PAINTING OR COATING SURFACES

The present invention relates to paint or coating compositions, methods for painting or coating surfaces and the use of particular compositions for painting or coating particular structures.

TECHNICAL BACKGROUND

European Patent Application No. 79 104321.9 and the corresponding International Patent Application No. PCT/DK79/00047 discloses particular materials showing extremely valuable properties with respect to dense and durable structure and excellent shapeability in uncured state.

In the following specification and claims, these materials will be designated materials containing a "densified matrix". This term designates any coherent binder matrix disclosed in the above-mentioned patent applications. All of these binder matrices comprise

A) homogeneously arranged inorganic solid particles of a size of from about 50 Å to about 0.5 μ , or a coherent structure formed from such homogeneously arranged particles, and

B) densely packed solid particles having a size of the order of 0.5 - 100 μ and being at least one order of magnitude larger than the respective particles stated under A), or a coherent structure formed from such densely packed particles,

the particles A or the coherent structure formed therefrom being homogeneously distributed in the void volume between the particles B,

the dense packing being substantially a packing corresponding to the one obtainable by gentle mechanical influence on a system of



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geometrically equally shaped large particles in which locking surface forces do not have any significant effect.

As described in the above-mentioned patent applications, additional bodies which have at least one dimension which is at least one order of magnitude larger than the particles A may be embedded in the matrix. Such additional are termed "bodies C" in International Patent Application NO. PCT/DK79/00047 and comprise a wide variety of bodies, including particles such as sand or stone and fibers such as, e.g., glass fibers, steel fibers, and plastics fibers.

10 In the following specification and claims, the term "a material comprising the densified matrix" designates any material having the densified matrix as a binder matrix and optionally containing bodies C as defined above.

As discussed in the above-mentioned patent applications, the particles B are preferably Portland cement particles, and the particles A are preferably ultrafine silica particles ("silica dust") having a specific surface area of about 50,000 - 2,000,000 cm²/g, preferably about 250,000 cm²/g, and preferred silica particles are described in detail in the said patent applications and comprise, e.g., particles by growth from liquid or preferably vapour phase such as particles formed as a byproduct in the production of ferrosilicium or silicium metal in electrical furnaces. As described in the above-mentioned patent applications, articles comprising the densified matrix may be made from an easily flowable composite material of an extremely low liquid content by shaping in a low stress field. In the following specification and claims, the term "composite material" designates any composite material which, on curing, forms a material comprising the densified matrix. These composite materials are described in great detail in the above-mentioned patent applications. The composite material containing Portland cement particles as particles B comprises an extremely high amount of a dispersing agent, typically a concrete superplasticizer, and examples of useful concrete superplasticizers are given in the above-mentioned patent applications. Methods and materials for producing, casting and further treating the densified matrix

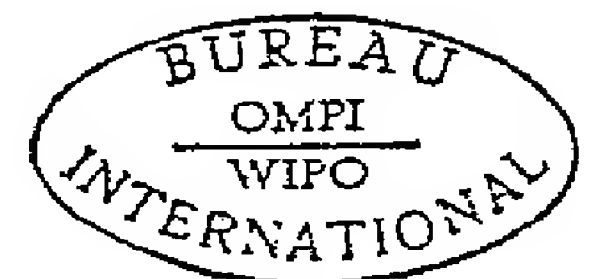


as disclosed in the above-mentioned patent applications are also useful for producing the densified matrix in the context of the present application.

In the following specification and claims, the term "densely packed" is to be understood in accordance with the definition of "dense packing" given above.

DESCRIPTION OF THE PRESENT INVENTION.

According to one aspect of the present invention, the densified matrix is utilized as protective coating for application on particular surfaces to be protected, in particular steel surfaces. In this utilization of the densified matrix, the density of the matrix with its inherent mechanical properties is utilized. When the surfaces to be protected are, e.g., surfaces to be protected against corrosion, in particular steel surfaces, the particles B preferably comprise cement particles, in particular Portland cement particles, or at least a major proportion of cement particles, in particular Portland cement particles, thereby resulting in a paint which has the well-known rust-prevention properties of cement-containing paints. Surfaces which are suitably protected by means of such paint are, e.g., steel surfaces in ballast tanks, cargo holds, cofferdams, and other surfaces, especially on ship hulls or other marine structures, particularly in or on ships, or offshore structures, where rust prevention or resistance to other kinds of corrosion is to be obtained, including bridge undersides, the interior of offshore legs, ship cabins; ship decks and aircraft landing areas on ships or other constructions. Other structures which are protected by means of the paints or surface coatings comprising the densified matrix are drinking water tanks, underseals for containers, and jacketing for pipelines, etc. Also, ship structures such as cabin walls which are to be supplied with a superimposed insulating layer such as a layer of Rockwool® are typical surfaces being treated with the paints or surface coatings comprising the dense matrix. The present invention is not restricted to the use of the materials comprising the densified matrix in or on marine or offshore structures;

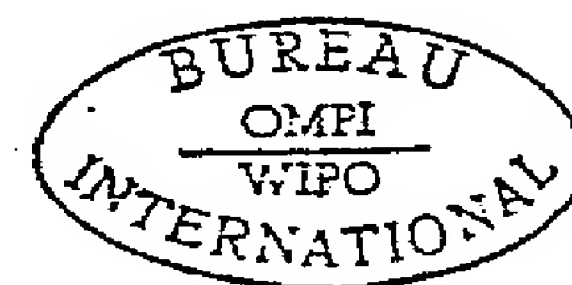


also the painting or coating of other structures, including industrial plants, containers, buildings, etc. is within the scope of the present invention.

When used as a paint or surface coating for application on the above-mentioned surfaces or similar surfaces, the composite material is preferably adapted to obtain optimum adhesion to the surface to be painted or protected, ordinarily a steel surface, and is suitably modified to further enhance its adhesion to the surface and to improve the application properties of the paint and the flexibility and resistance against cracking of the final paint layer. According to the invention, this modification is performed by addition of additives of organic or inorganic character. Important additives are organic or inorganic binders, thixotropic agents, co-solvents, defoamers, dispersing agents, pigments, and plasticizers.

According to one of the main aspects of the present invention, the composite material or paint of the invention comprises - in addition to the components resulting in the formation of a densified matrix comprising particles A, B, and optionally C - an organic binder. The organic binder is suitably incorporated as a water-based emulsion such as an acrylic emulsion, polyvinylacetate emulsion, polyvinylidene chloride emulsion, acryl-styrene emulsion, styrene-butadiene emulsion, polyvinyl chloride emulsion, wax emulsion, polyethylene derivative emulsion, polyvinylidene-butadiene emulsion, or vinylacryl emulsion. Such emulsions are incorporated in an amount of typically 5 - 60% by weight, preferably, to obtain maximum flexibility, 20 - 40% by weight, calculated on the dry matter content of the emulsion and the total dry matter content of the composition; a suitable compromise between adequate flexibility and economy of the composition is often obtained when the emulsion is incorporated in an amount of about 5 - 25% by weight, calculated on the same basis.

Other suitable modifying agents are thixotropic agents for improvement of the flowing properties of the paint, permitting the obtainment of thicker layers of the paint applied. The thixotropic agents are typically added in an amount of 0.5 - 10% by weight, preferably 1 -



5% by weight, calculated on thixotropic agent dry matter and the total dry matter of the paint. Typical thixotropic agents are

Mineral thixotropic agents, including

silicas

5 bentonites and

attapulgites

vegetable thixotropic agents, including

cellulose,

starch,

10 dextrin,

alginates,

castor oil derivatives

natural gums,

thixotropic agents of animal origin, including

15 gelatine,

glue,

casein,

synthetic thixotropic agents, including

synthetic cellulose derivatives including starch acetate,

20 polyvinyl alcohols,

polyvinylpyrrolidone,

polyvinylether derivatives,

polyacrylamides,

polyurethanes.

25 When the paint of the invention contains an incorporated organic binder, e.g. a binder in the form of an emulsion as described above, an interesting embodiment of the invention comprises incorporating a "co-solvent" in the form of a water-miscible organic solvent in an amount of 1 - 5% by weight, calculated on the dry matter of the

30 paint. Examples of co-solvents are glycolethers, e.g. ethoxyethanol, butoxyethanol (also termed "butylglycol"), glycoletheracetates, e.g. diethyleneglycolmonobutylether acetate (also termed "butyldiglycol acetate") and esters of carboxylic acids such as 2,2,4-trimethyl-1,3-pentanediol-monoisobutyrate ("Texanol" from Eastman Kodak, USA).

35 These co-solvents exert their effect when the water originally present



in the composite material gradually reacts, thus leaving a gradually increasing concentration of the solvent in the remaining liquid phase. The solvent thus gradually concentrated tends to migrate in the composite material and swell and coalesce the particles of emulsified binder, which tends to improve the flowing and film-forming properties of the paint and to result in a film which is substantially free of any pores.

In addition to binders which are of the emulsion type as exemplified above, it is also possible to use binders of the types which are soluble in water/alcohol mixtures and incorporate alcohol in the water phase of the paint. Such combination can be used to secure a relatively fast drying of the paint surface as the alcohol evaporates, thereby securing that the water present beneath the dried surface is prevented from evaporating and is thus retained for the desired reaction with the inorganic binder. Binders soluble in water/alcohol mixtures and contemplated for this purpose are, e.g., alkyds, allyl-ethers, acrylics, and styrene-maleic acid polymers. Such binders are used in the same amount as stated above for binders in emulsified form.

According to another aspect of the present invention, the paint incorporates small amounts, e.g. 0.01 - 5% by weight, calculated on the total dry matter content of the paint, of defoaming agents such as silicone-containing defoamers, e.g., "Tegopren K 133" from Goldschmidt, Essen, Federal Republic of Germany, or silicone-free defoaming agents, e.g., fatty acid derivatives such as "Bevaloid 688" or "Bevaloid 581B" from "Bevaloid Ltd., Yorkshire, England, or "Nopco NXZ" or "Nopco 8034" from Diamond Shamrock Corporation, Wilmington, Delaware, U.S.A. The defoaming agents prevent the incorporation of air during the formulation, mixing and application of the paint, thus avoiding air voids in the dry coating.

The compositions used for the purpose of the present invention will usually have a liquid:powder ratio in the range of about 0.20 - 0.45 or even 0.50 by weight, in particular in the range of 0.23 - 0.40, especially 0.27 - 0.38 by weight. (When the liquid is an emulsion, the



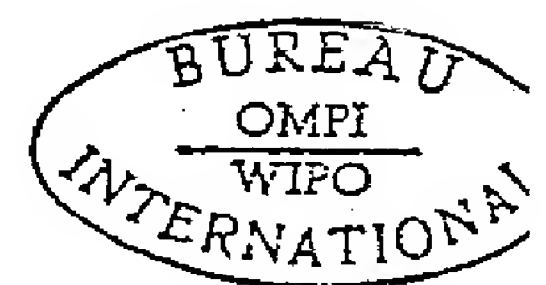
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binder content thereof is considered as pertaining to the powder and will normally be in the size range defined for particles A.)

According to a particular aspect of the invention, the paint incorporating the densified matrix is prevented from premature curing or setting by using, instead of the water in the usual embodiment of the composite material disclosed in the above-mentioned patent application, a water-miscible liquid such as a glycol, e.g., ethylene glycol or propylene glycol. In this manner, the paint may be produced and shipped in the "glycol form" where substantially no curing of the inorganic binder takes place. When the paint is applied on a wet surface, or is applied on a surface which is thereafter wetted, the glycol is partially replaced with water, thus resulting in curing of the inorganic binder.

According to a particular embodiment of the present invention, the paint is formulated as an antifouling paint for application of ship hulls, offshore structures, or other marine structures. For this purpose, antifouling agents are incorporated in the paint. The antifouling agents may be in the form of particles (normally of the size corresponding to particles B) such as cuprous oxide or zinc oxide, or they may be in the form of liquid antifouling agents. Particularly interesting antifouling agents are tin compounds of the general formula R_3SnX wherein each R is a hydrocarbon group such as phenyl, benzyl, propyl, butyl, pentyl, octyl, or nonyl and X is an acid residue of a mineral or organic acid such as chloride, fluoride or acetate, or X is the acid residue of a polymeric acid such as polyacrylic acid. Examples of such tin compounds are triphenyltin chloride, triphenyltin fluoride, tributyltin fluoride, or tributyltin chloride. As an example of a liquid antifouling agent may be mentioned tributyltin oxide. The antifouling paint according to the invention may also be formulated with a content of a herbicide such as Diuron or antimicrobial enzymes such as protease, esterase, or cellulase to control fouling organisms.

The paint of the present invention is useful not only for normal application methods such as airless or air spraying, brushing, or



rolling, but also for application under water or in the splash zone by brushing, by means of brooms, by means of rollers, or by spraying.

In some cases, it may be desirable to perform a pre-treatment of the surface on which the paint of the invention is to be applied, in order to increase the adhesion of the paint to the surface and enhance the protective efficiency of the paint. Examples of suitable pre-treatments are: Treatment with acids such as sulphuric acid or phosphoric acid, treatment with bacteria such as sulfate-reducing and iron-oxidizing bacteria, dry or wet blasting with sand or grit, mechanical cleaning of the surface, such as scraping, hammering, or high pressure washing. One of the major advantages of the paint of the invention is that it can be effectively applied on a moist surface.

When used in dark environments, such as ballast tanks, etc, the paint of the invention is suitably composed in such a manner that it has a substantially light colour so that it is easier to visually assess what surfaces have been treated. This may be obtained by incorporating pigments as part of particles B, e.g., zinc oxide or titanium dioxide, or by using particles A which are of a light colour, such as white silica particles derived from the production of silicium and/or ferrosilicium in electrical furnaces.

On the other hand, the composition of the invention may be prepared in almost any desired colour. Thus, e.g., using white cement and tinting pastes, red, green, blue and black samples have been prepared.

In order to improve the cracking resistance of the paint of the invention, special pigments, including pigments of a plate-shaped character such as mica or asbestine, aluminum, micaceous iron oxide, or fibers, including asbestos, chrysotil, graphite, basalt, polyethylene, cellulosic fibers, etc. may be incorporated as bodies C.

In principle the composite material constituting the paint or coating composition of the present invention is prepared from particles A, particles B, a liquid, a surface-active dispersing agent and optionally



additional bodies C in the same manner as disclosed in the above-mentioned patent applications. It is important that the amount of particles B substantially corresponds to dense packing thereof in the composite material with homogeneously packed or preferably densely packed particles A in the voids between the particles B and that the amount of liquid substantially corresponds to the amount necessary to fill the voids between particles A and B, and further, that the amount of dispersing agent is sufficient to impart, to the composite material, a fluid to plastic consistency in a low stress field of less than 5 kg/cm², preferably less than 100 g/cm². The additional constituents incorporated in accordance with most aspects of the present invention, such as binders, thixotropic agents, and defoamers, are incorporated by methods adapted in accordance with the character of the particular constituent. When the binder is a binder in the form of an emulsion, the emulsion *per se* is used as part of or as the whole liquid constituent for preparing the composite material. When the additional components are added in powder form, these are suitably either mixed with the dry constituents before addition of liquid, or are incorporated during the mixing, after the liquid or part of the liquid has been added, or they may be added in a form where they are dissolved or dispersed in liquid. As stated above, the liquid will normally be water, but it will be understood that it is also within the scope of the invention to use glycol or a glycol/water mixture as the liquid in order to obtain retardation of the curing of the inorganic binder, and it is also within the scope of the invention to incorporate, e.g., alcohol or another organic solvent in order to coalesce or dissolve an incorporated organic binder in accordance with the principles discussed above.

In the preparation of the composite material constituting the paint or coating composition of the present invention, the dry constituents thereof may be mixed in any desired manner. Thus, e.g., the particles B, typically Portland cement, may be mixed with the particles A, and the resulting mixture may be admixed with any added dry constituents such as particles C and/or binder, thixotropic agent, or defoamer, or the particles A may be mixed with any other dry constituents to be added, such as binder, thixotropic agent, or de-



foamer, and thereafter mixed with the particles B and optionally particles C. When the particles B comprise, e.g., Portland cement, an interesting mixing sequence is to mix all other constituents than the Portland cement, including particles A, added binder (when the binder is not constituted by the particles A), optionally thixotropic agents and defoamers, and optional Particles C and liquid, optionally including coalescing agent or a glycol, and then to add the cement to this mixture at the application site, preferably immediately before the application of the paint. In all embodiments of the formulation of the paint, care must be taken to obtain a homogeneous mixture showing the essential characteristics of the materials resulting in the densified matrix, cf. the above-mentioned patent applications.

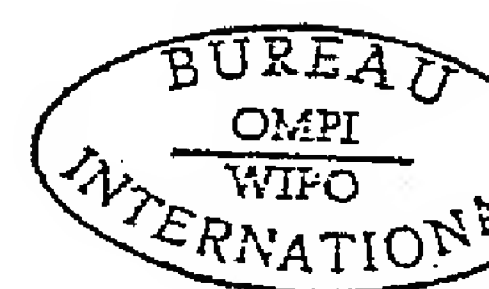
The invention is now further illustrated with reference to the drawing, in which

- Fig. 1 illustrates the size distribution of Portland cement, silica, and acrylic emulsion, respectively, and Fig. 2 illustrates the packing density of compositions with varying cement/silica ratios with 15 parts by weight of acrylic emulsion and without acrylic emulsion ("Acronal" S 702 from BASF), respectively.
- Both curves in Fig. 2 are calculated theoretically on the basis of the particle size distribution illustrated in Fig. 1. As appears from Fig. 2, the maximum density of the composition containing 15% of acrylic emulsion is obtained at a silica content of 10 g of silica per 90 g of cement, whereas the necessary amount of silica to obtain dense packing without the emulsion is more than 20 g of silica per 80 g of cement. As will appear from the examples which follow, the best results are obtained at the maximum density of the emulsion-containing composition.

EXAMPLE A

30 Compatibility of Various Emulsion Types with Cement

In order to assess the compatibility between pure cement and various



types of emulsions contemplated for the purpose of the present invention, a series of experiments was performed. Various emulsion types were added to cement powder, whereafter water and optionally defoamer were added. The ingredients and ratios appear from Table 1.

Table 1.
Various-Emulsion Types in Cement

Formula No.	Latex type	Addition w/w pph on cement	De-foamer ⁴	Water/solids ratio	Viscosity Krebs Units
1	Acrylic ¹	10	-	0.28	108
2		25	-	0.20	104
3	Styrene butadiene ²	10	+	0.33	paste
4		25	+	0.20	102
5	Vinyl ³	10	+	0.48	108
6		25	+	0.42	paste

- 1 = Acronal S 702 from BASF
 2 = Litex CA from Hüls
 3 = Vinamul 6705 from Scado
 4 = Nopco NXD from Diamond Shamrock
 pph = parts per hundred

In all of the experiments, a stable mixture was obtained, which shows that there is full compatibility between these different latex emulsion types and the cement. Although the remaining working examples all use the acrylic latex type, (which is the preferred latex type because it results in the best fiber formation), the results of the present experiments show that the other types of latex emulsion may also be used for the purpose of the present invention.



EXAMPLE 1

Formulations of densified cement matrices with acrylic emulsion, added in an amount ranging from 10 to 50 pph, were prepared. The ingredients and their ratios appear from Table 2.

5

. . . Table 2

Addition of Acrylic Emulsion to Densely Packed Cement

	Formula No.	Cement	Silica ¹	Acronal	Plasticizer ²	Retarder ³
		g	g	g	g	g
10	7	80	20	10	1.6	-
	8	80	20	15	1.6	-
	9	80	20	25	1.6	-
	10	80	20	30	1.6	-
15	11	80	20	50	1.6	-
	12	95	5	15	-	0.1
	13	90	10	15	-	0.1
	14	80	20	15	-	0.1
	15	80	20	15	1.6	0.1
20						



(Table 2 continued):

Formula no.	Water/ solids ratio	Viscosity Krebs Units	Pot-life ⁴	Film Formation	
				Cured at ambient con- ditions	Cured at 100% R.H.
5					
	7	0.26	108	~20 min.	crack OK
	8	0.26	110	~20 min.	crack OK
10	9	0.26	108	1/2 hour	crack OK
	10	0.27	104	1/2 hour	crack OK
	11	0.28	106	1/2 hour	crack OK
	12	0.26	108	1 hour	OK OK
	13	0.24	116	1/2 hour	micro-crack OK
15	14	>0.40	paste		
	15	0.28	100	1 hour	crack OK

1 = Silica 100 from Elkem

2 = Mighty

20 3 = Natrosol 250 LR from Hercules

4 = Time until viscosity reaches 130 Krebs Units

25 The products were prepared in the same manner as in Example A, the cement and the silica being dry mixed before addition of the emulsion. The emulsion was added in varying amounts. In all cases, excellent paint properties with respect to viscosity, pot life and film formation (when curing at 100% relative humidity) were obtained, such as appears from Table 2.

EXAMPLE 2

Influence of the Amount of Fine Powder

30 Three compositions of the same type as described in Example 1 were prepared, with varying amount of silica. The compositions were pre-



pared in the same manner as described in Example 1. The the proportions of ingredients and the results obtained appear from Table 3.

Table 3
Water/Solids Ratio

5	Formula No.	Cement g	Silica g	Acronal g	Plastizer ¹ g	Water/solids ratio	Viscosity Krebs Units
10	16	95	5	15	0.15	0.23	100
	17	90	10	15	0.15	0.33	100
	18	80	20	15	0.15	0.50	110

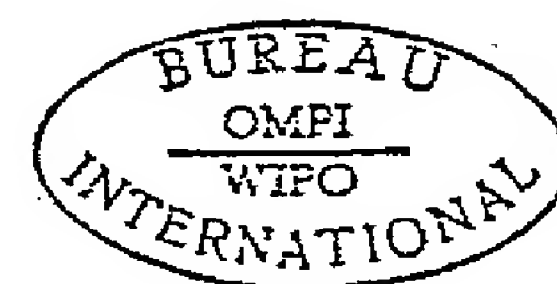
1 = Kleenoplast from Akzo

- 15 It will be noted that in order to obtain the same viscosity with varying amounts of silica, different amounts of water were used. In all cases, excellent paints were obtained.

EXAMPLE 3

Application of Compositions of the Invention on Steel Surfaces

- 20 Two compositions of the invention were applied on steel panels by means of a conventional spray technique, using a pistol GFG-50 from DeVill Biss, nozzle 0.030". The ingredients and their relative ratios, etc. appear from Table 4 in which "Sa 3" and "St 3" indicate the degree of cleanness of the steel according to Swedish Standard No.
- 25 SIS 055900-1967. For determination of the anti-corrosion properties of the compositions, the panels with the compositions were immersed in sea water for 3 months at Kyndby, Denmark. The results of this test appear from Table 4.



Other application methods which have been tested in practice and found to be suitable are pressure pot application using a PQM 5499 equipment from DeVill Biss, nozzle 0.064", or hoppergun application, using an equipment from Joc, Sweden.

5

Table 4
Compositions Immersed in Seawater for 3 Months

Formula No.	Cement g	Silica g	Acronal g	Plasti-cizer ¹ g	Fibres ² g	Retar-der ³ g	Water/solids ratio
19	80	20	-	1.6	6	-	0.24
20	90	10	15	-	-	0.1	0.38

15

20

25

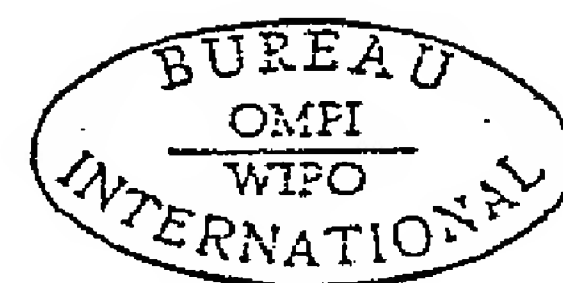
19	Seawater Immersion	
	Blistering ⁴	Rust ⁴
Sa 3	10	10
St 3	10	10
20	Seawater Immersion	
	Blistering ⁴	Rust ⁴
Sa 3	10	10
St 3	10	10

1 = Mighty

2 = Rockwool FPX from Rockwool

30 3 = Natrosol 250 LR from Hercules

4 = Scale from 0 to 10, 10 best



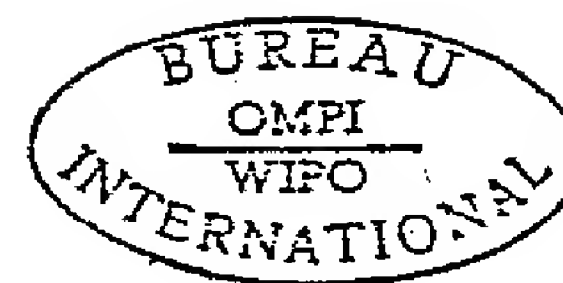
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As appears from Table 4, the coating was non-blistering and gave maximum rust protection in all cases.

EXAMPLE 4

5 A number of fiber-containing compositions of the invention were made in the same manner as described in Example 2; the fibers were added together with the water.

The amounts of the ingredients and the results obtained appear from Table 5.



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Table 5
Addition of Fibres

5	Formula	Cement	Silica	Acro-	Plasti-	Fibre	Retarder ²⁾
	No.			nal	cizer ¹⁾	Type Amount	
		g	g	g	g	g	g
10	21	90	10	15	1.8	4)	6 0.1
	22	90	10	15	1.8	4)	4 0.1
	23	90	10	15	1.8	4)	2 0.1
	24	90	10	15	1.8	5)	6 0.1
	25	90	10	15	1.8	5)	4 0.1
	26	95	5	15	1.9	5)	6 0.1
	27	95	5	15	1.9	5)	4 0.1
15	Formula	Water/so-	Viscosity	Pot-life ³⁾	Film Formation		
	No.	lids ratio	Krebs Units		Cured at am- bient condi- tions	Cured at 100% R.H.	
20	21	0.32	112	~1/2 h	OK	OK	
	22	0.29	106	~1/2 h	OK	OK	
	23	0.28	114	~1/2 h	crack	OK	
	24	0.26	108	~1/2 h	crack	OK	
25	25	0.27	104	~1/2 h	crack	OK	
	26	0.27	100	1/2 h	OK	OK	
	27	0.27	108	1/2 h	OK	OK	

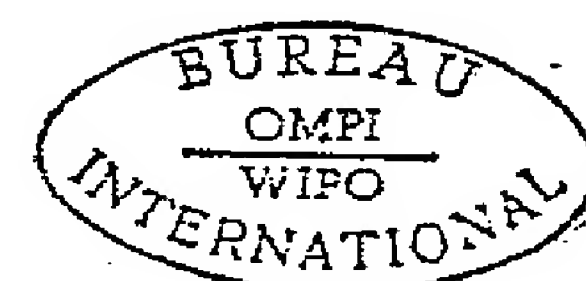
1) Mighty

30 2) Natrosol 250 LR from Hercules

3) Time until viscosity reaches 130 Krebs Units

4) Rockwool FPX from Rockwool

5) Wollastonite from Nyco



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In all cases, good film formation was obtained by comparing the results stated in Table 5 with the data apparent from Table 2, it will be noted that the incorporation of fibers results in a considerable increase in the resistance to crack when the film is cured at ambient
5 conditions.

EXAMPLE 5

Effect of Incorporation of Plasticizer

Various compositions were made using the ratios of ingredients stated in Table 6. The method was the same as described in Example 2.



- 19 -

Table 6
Incorporation of Plasticizer

5	Formula	Cement	Silica	Acronal	Plasticizer		Natrosol
	No.				Type	Amount	250 LR
		g	g	g		g	g
10	28	80	20	-	-	-	-
	29	80	20	15	-	-	-
	30	80	20	0	2)	3.2	-
	31	80	20	15	2)	1.6	0.1
	32	80	20	15	2)	3.2	0.1
	33	80	20	15	3)	3.2	-
	8	80	20	15	4)	1.6	-
15	Formula	Water/solids	Viscosity	Pot-life ¹⁾	Film Formation		
	No.	ratio	Krebs Unit		Cured at	Cured at	
					ambient	100% R.H.	
					conditions		
20	28	>50	Dry lumps				
	29	>40	Paste				
	30	0.23	100	10 m	crack	OK	
	31	0.39	Thixotropic	~1/2 h	crack	OK	
25	32	0.30	100	20 m	crack	OK	
	33	0.28	100	~1/2 h	crack	OK	
	8	0.26	110	~20 m	crack	OK	

1) Time until viscosity reaches 130 Krebs Units

30 2) Darachem from Grace

3) Sikament from Sika-Beton

4) Mighty



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It will be noted from Table 6 that the incorporation of a plasticizer in a high amount is essential to the obtainment of a composition according to the invention: in the two cases where the plasticizer was omitted, it was not possible to obtain a workable composition.

5 EXAMPLE 7

Influence of Retarders on Pot Life

10 In the same manner as described in Example 2, various compositions were prepared with and without retarder; the compositions and the results obtained appear from Table 7. In all cases, the retarder showed good compatibility with the other constituents of the composition. It will be noted that the incorporation of the retarder resulted in a considerably increased pot life.



Table 7
Influence of Retarders

5	Formula No.	Cement	Silica	Acronal	Plasti- cizer ¹⁾	Retarder	
		g	g	g	g	Type	Amount g
10	34	100	0	15	1.6	-	-
	35	90	10	15	1.6	-	-
	36	100	0	15	-	3)	0.1
	37	95	5	15	-	3)	0.1
	38	90	10	15	-	3)	0.1
	39	90	10	15	1.8	4)	0.1
15	Formula No.	Water/solids ratio		Viscosity Krebs Units	Pot-life ²⁾	Film Formation	
						Cured at ambient conditions	Cured at 100% R.H.
20	34	0.21		110	10 m	OK	OK
	35	0.22		112	15 m	crack	
	36	0.26		114	1 h	OK	
	37	0.26		108	1 h	OK	OK
	38	0.24		116	1/2 h	micro-crack	OK
25	39	0.29		110		edge crack	OK

1) Mighty

2) Time until viscosity reaches 130 Krebs Units

3) Natrosol 250 LR from Hercules

30 4) Natrosol 250 HHR from Hercules



CLAIMS

1. A method for painting or coating steel surfaces in ballast tanks, cargo holds, cofferdams, bridge undersides, the interior of offshore legs, ship hulls, ship cabin walls, ship decks, aircraft landing areas on ships or offshore constructions, drinking water tanks, underseals for containers, etc., comprising applying a composite material which, on curing, forms a material comprising a matrix comprising

10 A) homogeneously arranged inorganic solid particles of a size of from about 50 Å to about 0.5 μ, or a coherent structure formed from such homogeneously arranged particles, and

B) densely packed solid particles having a size of the order of 0.5 - 100 μ and being at least one order of magnitude larger than the respective particles stated under A), or a coherent structure formed from such densely packed particles,

15 the particles A or the coherent structure formed therefrom being homogeneously distributed in the void volume between the particles B,

20 the dense packing being substantially a packing corresponding to the one obtainable by gentle mechanical influence on a system of geometrically equally shaped large particles in which locking surface forces do not have any significant effect,

and allowing the paint or surface coating composition to cure to form the above-defined matrix.

25 2. A method according to claim 1 wherein the particles B are particles which cure by partial dissolution in a liquid, chemical reaction in the dissolved phase, and precipitation of a reaction product.

30 3. A method according to any of the preceding claims wherein the particles A are particles which cure by partial dissolution in a liquid, chemical reaction in the solution, and precipitation of a reaction product.



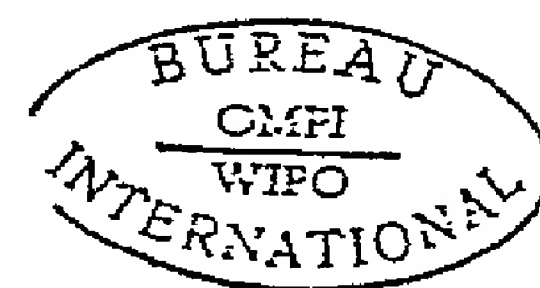
- 23 -

4. A method as claimed in claims 2 and 3 wherein the particles A show a substantially lower reactivity than the particles B, or substantially no reactivity.
5. A method according to any of the preceding claims wherein the particles B comprise at least 50% by weight of Portland cement particles.
6. A method as claimed in any of the preceding claims wherein the particles A are particles of silica dust having a specific surface area of about 50,000 - 2,000,000 cm²/g, in particular about 250,000 cm²/g.
7. A method according to claim 6 wherein the silica dust particles are present in an volume which is about 0.1 - 50% by volume, preferably 5 - 50% by volume, in particular 10 - 30% by volume, of the total volume of particles A + B.
8. A modification of the method according to any of claims 1 - 7 for painting or coating the structures stated in claim 1 or other marine, offshore or land structures to be coated and/or protected, comprising applying a paint or surface coating composition as stated in claim 1 which additionally contains an organic binder and optionally a defoamer and/or a thixotropic agent, and allowing the paint or surface coating composition to cure to form the above-defined matrix.
9. A method according to claim 8 wherein the organic binder is a water-based emulsion.
10. A method according to claim 9 wherein the emulsion is an acrylic emulsion, polyvinylacetate emulsion, polyvinylidene chloride emulsion, acryl-styrene emulsion, styrene-butadiene emulsion, polyvinyl chloride emulsion, wax emulsion, polyethylene derivative emulsion, polyvinylidene-butadiene emulsion, or vinylacryl emulsion.
11. A method according to claims 9 or 10 wherein the emulsion is present in the paint or surface coating composition in an amount of 5 - 60% by weight, preferably 20 - 40% by weight, calculated on



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15. A method according to any of claims 8 - 11 wherein the paint or surface coating composition comprises a water-miscible organic solvent in an amount of 1 - 5% by weight, calculated on the dry matter of the paint.
- 5 16. A method according to claim 15 wherein the organic solvent is selected from the group consisting of glycolethers, e.g. ethoxyethanol, butoxyethanol, glycoletheracetates, e.g. diethyleneglycolmonobutylether acetate and esters of carboxylic acids such as 2,2,4-trimethyl-1,3-pentanediol-monoisobutyrate.
- 10 17. A method according to any of the preceding claims wherein the paint or surface coating composition comprises 1) a binder which is soluble in water/ alcohol mixtures and 2) an alcohol/water mixture as the liquid.
- 15 18. A method according to claim 17 wherein the binder which is soluble in water/alcohol mixtures is selected from alkyds, allylethers, acrylics, and styrene-maleic acid polymers.
- 20 19. A method according to claim 18 wherein the binder soluble in water/alcohol mixtures is present in an amount of 5 - 60% by weight, preferably 20 - 40% by weight and especially 5 - 25% by weight, calculated on the dry matter content of the composition.
- 25 20. A method according to any of the preceding claims wherein the paint or surface coating composition incorporates small amounts, e.g. 0.01 - 5% by weight, calculated on the total dry matter content of the paint, of defoaming agents such as silicone-containing defoamers; or silicone-free defoaming agents, e.g., fatty acid derivatives.
- 30 21. A method according to any of the preceding claims wherein the paint or surface coating composition has a liquid:powder ratio in the range of about 0.20 - 0.45 by weight, in particular in the range of 0.23 - 0.40, especially 0.27 - 0.38, by weight, the organic binder content of any binder emulsion present in the composition being considered as pertaining to the powder.



the dry matter content of the emulsion and the total dry matter content of the composition.

12. A method according to any of the preceding claims wherein the paint or surface coating composition contains a thixotropic agent.

13. A method according to claim 12 wherein the thixotropic agent is present in the paint or surface coating composition in an amount of 0.5 - 10% by weight, preferably 1 - 5% by weight, calculated on thixotropic agent dry matter and the total dry matter of the paint.

14. A method according to claim 6 or 7 wherein the thixotropic agent is selected from

Mineral thixotropic agents, including

silicates

bentonites and

attapulgites

15 vegetable thixotropic agents, including

cellulose,

starch,

dextrin,

alginates,

20 castor oil derivatives

natural gums,

thixotropic agents of animal origin, including

gelatine,

glue,

25 casein,

synthetic thixotropic agents, including

synthetic cellulose derivatives including starch acetate,

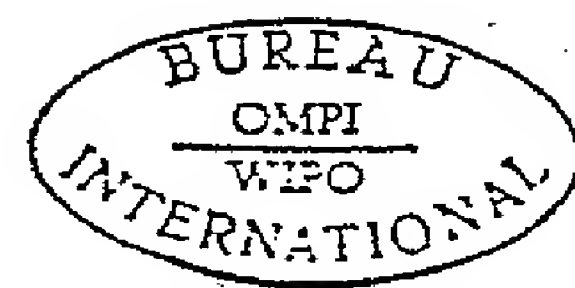
polyvinyl alcohols,

polyvinylpyrrolidone,

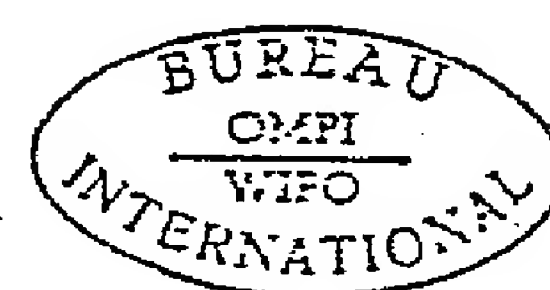
30 polyvinylether derivatives,

polyacrylamides,

polyurethanes.



22. A modification of the method according to any of the preceding claims for painting or coating the structures stated in claim 1 or other marine, offshore or land structures to be coated and/or protected, comprising applying a paint or surface coating composition as stated in claim 1 which contains, as the liquid phase thereof, a glycol or a mixture predominantly containing a glycol.
23. A method according to claim 22 wherein the glycol is ethylene glycol or propylene glycol.
24. A modification of the method according to any of the preceding claims for painting ship hulls, offshore structures, or other marine structures, comprising applying a paint or surface coating composition as stated in claim 1 or any other preceding claim containing an anti-fouling agent.
25. A method as claimed in claim 24 wherein the antifouling agents is in the form of particles corresponding to particles B, such a cuprous oxide or zinc oxide, or organic tin compounds of the formula R_3SnX wherein each R is a hydrocarbon group such as phenyl, benzyl, propyl, butyl, pentyl, octyl, or nonyl, e.g. triphenyltin chloride, triphenyltin fluoride, tributyltin fluoride, or tributyltin chloride.
26. A method according to claim 24 wherein the antifouling agent incorporated in the paint or surface coating composition is a liquid antifouling agents such as tributyltin oxide.
27. A method according to any of the preceding claims wherein the paint or surface coating composition is applied by airless or air spraying, brushing, or rolling.
28. A method according to any of the preceding claims wherein the paint or surface coating composition is applied on a marine or offshore structure by application under water or in the splash zone by brushing, by means of brooms, by means of rollers, or by spraying.



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29. A method according to any of the preceding claims wherein the surface on which the paint or surface coating composition is to be applied, is pre-treated with acids such as sulphuric acid or phosphoric acid, with bacteria such as sulfate-reducing and iron-oxidizing bacteria, by dry or wet blasting with sand or grit, by mechanical cleaning of the surface, such as scraping, hammering, or by high pressure washing.

30. A method according to any of the preceding claims wherein the paint or surface coating composition contains a pigments as part of particles B, e.g., zinc oxide or titanium dioxide, or contains particles A which are of a light colour, such as white fly ash particles derived from the production of silicium and/or ferrosilicium in electrical furnaces.

31. A method according to any of the preceding claims wherein the paint or surface coating composition contains pigments of a plate-shaped character such as mica or asbestine, aluminum, micaceous iron oxide, or fibers, including asbestos, chrysotil, graphite, basalt, polyethylene, or cellulosic fibers.

32. A paint or surface coating composition comprising

20 A) inorganic particles of a size of from about 50 Å to about 0.5 μ, and

B) solid particles having a size of the order of 0.5 - 100 μ, and being at least one order of magnitude larger than the respective particles stated under A),

25 a liquid,

and a surface-active dispersing agent,

the amount of particles B substantially corresponding to dense packing thereof in the composite material with homogeneously packed particles A in the voids between particles B, the amount of liquid



substantially corresponding to the amount necessary to fill out the voids between particles A and B, and the amount of dispersing agent being sufficient to impart to the composite material a fluid to plastic consistency in a low stress field of less than 5 kg/cm^2 , preferably
5 less than 100 g/cm^2 ,

and optionally

C) additional bodies which have at least one dimension which is at least one order of magnitude larger than the particles a),

and additionally an organic binder and optionally a defoamer and/or a
10 thixotropic agent.

33. A paint as claimed in claim 32 showing the features stated in any of claims 8 - 31.

34. A method for preparing a paint or surface coating composition useful in the method as claimed in any of claims 1 - 21, comprising
15 mixing particles A, particles B, a liquid, a surface-active dispersing agent and optionally additional bodies, the amount of particles B substantially corresponding to dense packing thereof in the paint or surface coating composition with homogeneously packed or preferably densely packed particles A in the voids between the particles B, the
20 amount of liquid substantially corresponding to the amount necessary to fill the voids between particles A and B, and the amount of dispersing agent and the extent of mixing being sufficient to impart, to the paint or surface coating composition, a fluid to plastic consistency in a low stress field of less than 5 kg/cm^2 , preferably less than 100
25 g/cm^2 , and, additionally incorporating an organic binder, a thixotropic agent, or a defoamer.

35. A method according to claim 34 wherein the binder in the form of an emulsion, and the emulsion *per se* is used as part of or as the whole liquid constituent for preparing the paint or surface coating
30 composition.



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36. A method as claimed in claim 34 or 35 wherein the particles A are mixed with the other dry constituents to be added, such as binder, thixotropic agent, or defoamer, except particles B, and are thereafter mixed with the particles B and optionally particles C.

- 5 37. A method according to claim 36 wherein the particles B comprise, Portland cement, and all other constituents than the Portland cement, including particles A, added binder (when the binder is not consti-
tuted by the particles A), optional thixotropic agents and defoamers,
and optional Particles C and liquid are mixed, optionally including
10 coalescing agent or a glycol, whereafter the cement is added to the resulting mixture at the application site, preferably immediately before the application of the paint or surface coating composition.



Fig. 1.

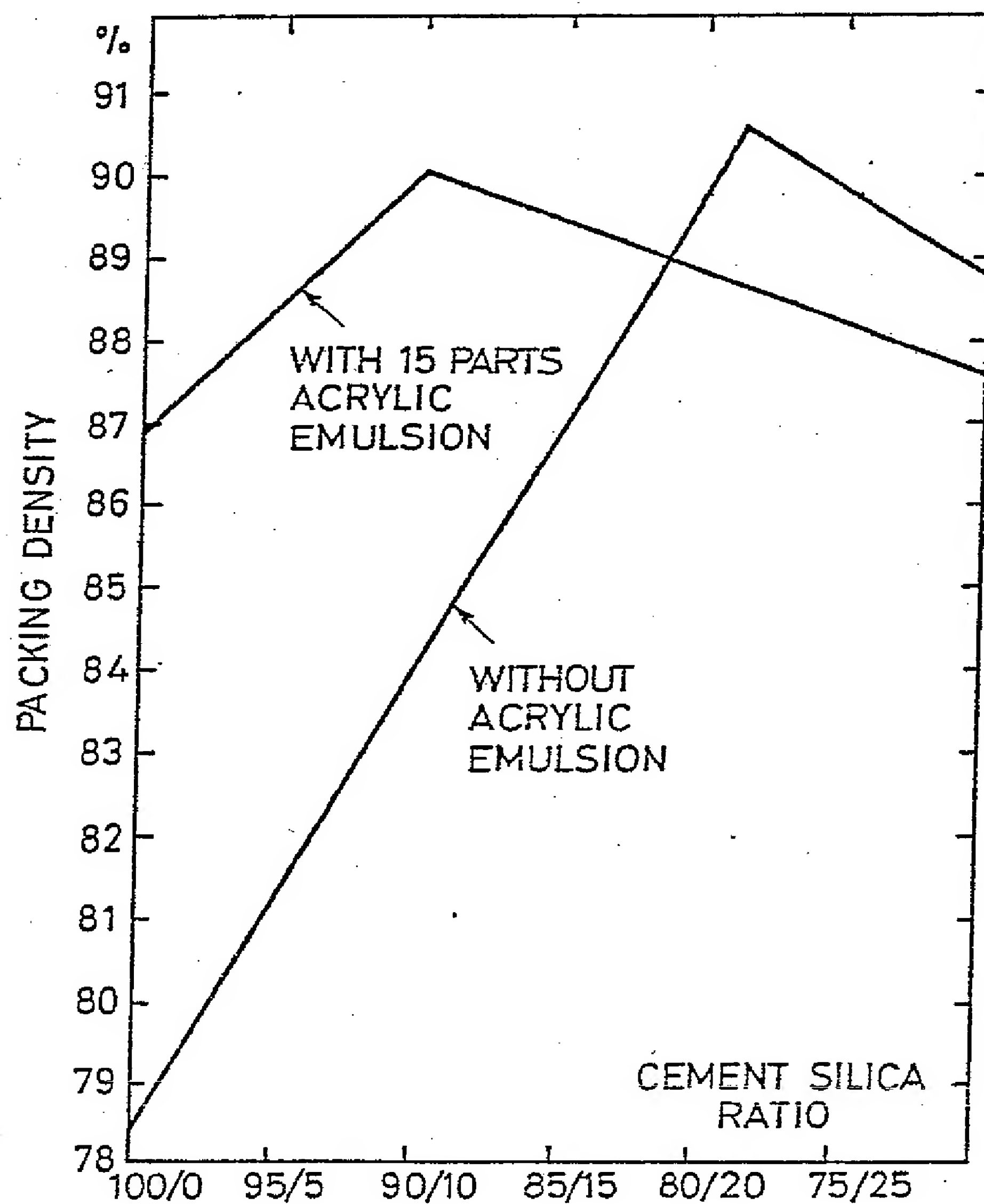
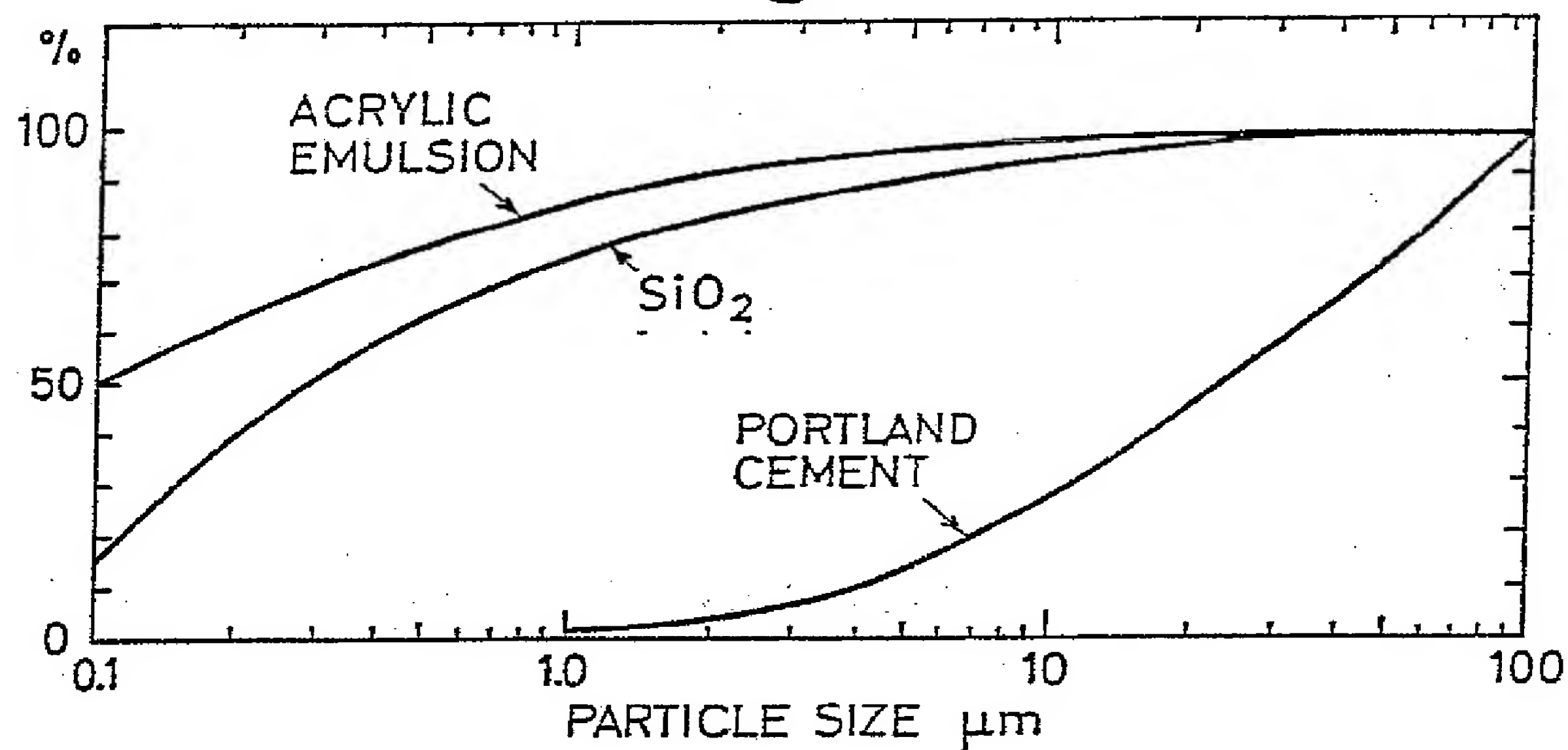


Fig. 2.



INTERNATIONAL SEARCH REPORT

International Application No. PCT/DK82/00012

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹ According to International Patent Classification (IPC) or to both National Classification and IPC ³ <div style="text-align: center; font-family: monospace; font-size: 1.2em;">C 04 B 31/00, C 09 D 5/00</div>																	
II. FIELDS SEARCHED <div style="text-align: right; font-size: 0.8em;">Minimum Documentation Searched ⁴</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border-bottom: 1px solid black; font-size: 0.8em;">Classification System</th> <th style="border-bottom: 1px solid black; font-size: 0.8em;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px; vertical-align: top;">IPC 2, 3</td> <td style="padding: 5px; vertical-align: top;">C 04 B 7/35, 13/00, 13/02, 13/04, 13/10, 13/21, 13/22, 13/24, 19/00, 19/02, 31/00-38, 35/66, 35/68, .../...</td> </tr> </table> <div style="text-align: center; font-size: 0.8em; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁶</div>			Classification System	Classification Symbols	IPC 2, 3	C 04 B 7/35, 13/00, 13/02, 13/04, 13/10, 13/21, 13/22, 13/24, 19/00, 19/02, 31/00-38, 35/66, 35/68, .../...											
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SE, NO, DK, FI classes as above																	
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border-bottom: 1px solid black; font-size: 0.8em;">Category [*]</th> <th style="border-bottom: 1px solid black; font-size: 0.8em;">Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷</th> <th style="border-bottom: 1px solid black; font-size: 0.8em;">Relevant to Claim No. ¹⁵</th> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="border-right: 1px solid black; padding: 5px; vertical-align: top;">EP, A, 10 777 (AKTIESELSKABET AALBORG PORTLAND-CEMENT-FABRIK) 14 May 1980 & WO, A, 80/00959 see p 20, lines 22-25, p 43, line 37 - p 44, line 5, p 74, claim 1, p 78, claim 28</td> <td style="padding: 5px; vertical-align: top;">1-8, 27, 30-34</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="border-right: 1px solid black; padding: 5px; vertical-align: top;">SE, B, 336 420 (E I DU PONT DE NEMOURS AND CO) 1 July 1968, see 5, lines 3-11, lines 21-22, 36-39</td> <td style="padding: 5px; vertical-align: top;">1, 12-14, 24, 25, 27, 29-31</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="border-right: 1px solid black; padding: 5px; vertical-align: top;">DE, B, 1 278 650 (AMERICAN PIPE AND CONSTRUCTION CO) 26 September 1968, see col 3, lines 19-21, 58-59; col 5, lines 53-57; col 9, lines 5-39</td> <td style="padding: 5px; vertical-align: top;">1, 8, 12-14, 24, 25, 29, 31</td> </tr> <tr> <td style="border-right: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="border-right: 1px solid black; padding: 5px; vertical-align: top;">DE, B, 1 280 726 (E I DU PONT DE NEMOURS AND CO) 17 October 1968, see col 1, lines 3-10; col 19, lines 48-52; col 20, lines 2-28; col 22, lines 37-61 <div style="text-align: right; margin-top: 10px;">.../...</div></td> <td style="padding: 5px; vertical-align: top;">1, 6-8, 13-14, 32-34</td> </tr> </table>			Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁵	X	EP, A, 10 777 (AKTIESELSKABET AALBORG PORTLAND-CEMENT-FABRIK) 14 May 1980 & WO, A, 80/00959 see p 20, lines 22-25, p 43, line 37 - p 44, line 5, p 74, claim 1, p 78, claim 28	1-8, 27, 30-34	X	SE, B, 336 420 (E I DU PONT DE NEMOURS AND CO) 1 July 1968, see 5, lines 3-11, lines 21-22, 36-39	1, 12-14, 24, 25, 27, 29-31	X	DE, B, 1 278 650 (AMERICAN PIPE AND CONSTRUCTION CO) 26 September 1968, see col 3, lines 19-21, 58-59; col 5, lines 53-57; col 9, lines 5-39	1, 8, 12-14, 24, 25, 29, 31	X	DE, B, 1 280 726 (E I DU PONT DE NEMOURS AND CO) 17 October 1968, see col 1, lines 3-10; col 19, lines 48-52; col 20, lines 2-28; col 22, lines 37-61 <div style="text-align: right; margin-top: 10px;">.../...</div>	1, 6-8, 13-14, 32-34
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁸</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search ² <div style="text-align: center; font-family: monospace;">1982-05-26</div> </td> <td style="width: 50%; border-bottom: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report ² <div style="text-align: center; font-family: monospace;">1982-05-11</div> </td> </tr> <tr> <td style="border-bottom: 1px solid black; padding: 5px;"> International Searching Authority ¹ <div style="text-align: center; font-family: monospace;">Swedish Patent Office</div> </td> <td style="border-bottom: 1px solid black; padding: 5px;"> Signature of Authorized Officer ¹⁰ <div style="text-align: center;"> Eva Ahlén </div> </td> </tr> </table>			Date of the Actual Completion of the International Search ² <div style="text-align: center; font-family: monospace;">1982-05-26</div>	Date of Mailing of this International Search Report ² <div style="text-align: center; font-family: monospace;">1982-05-11</div>	International Searching Authority ¹ <div style="text-align: center; font-family: monospace;">Swedish Patent Office</div>	Signature of Authorized Officer ¹⁰ <div style="text-align: center;"> Eva Ahlén </div>											
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International Searching Authority ¹ <div style="text-align: center; font-family: monospace;">Swedish Patent Office</div>	Signature of Authorized Officer ¹⁰ <div style="text-align: center;"> Eva Ahlén </div>																

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

II

Fields Searched (cont)IPC 2, 3 C 09 D 1/00, 1/02, 1/06, 5/00, 5/02,
5/04, 5/14, 5/16

C 23 F 5/00-5/04, 7/04

US Cl 106:14-16, 89, 97-99V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE ¹⁰

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____ because they relate to subject matter ¹¹ not required to be searched by this Authority, namely:2. ☐ Claim numbers _____, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹², specifically:VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING ¹³

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.☐ No protest accompanied the payment of additional search fees.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
X	DE, A, 2 752 803 (KANSAI PAINT CO LTD) 1 June 1978, see p 13, lines 3-5; p 16, line 1; p 19, lines 5-17; p 20, lines 14-16, line 20 - p 21, line 2	1, 6-8, 12-14, 20, 24, 25, 27, 31-34
X	DE, B, 1 519 098 (DAUBERT CHEMICAL CO) 19 March 1970, see col 1, lines 46-50; col 6, lines 40-68; col 7, lines 34-46	1, 8, 12-14, 20
X	US, A, 3 135 617 (W J NEWELL, J E MADDEN) 2 June 1964, see col 2, lines 33-35	1-7, 30
X	NO, B, 136 645 (ØYSTEIN RASMUSSEN) 4 July 1977	1, 24-26, 31
X	DE, B, 2 240 487 (SCHERING AG) 21 February 1974	1, 24-26
A	Paul Nylén, Edward Sunderland, Modern Surface Coatings, published 1965 by Spottiswoode, Ballantyne & Co Ltd (London) see p 378-383, in particular p 380	
P	H·H Bache, Densified Cement/Ultra-Fine Particle-Based Materials, June 10-12, 1981, The Second International Conference on Superplasticizers in Concrete, Ottawa, Canada, p 26	